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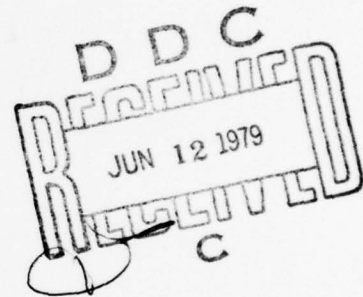
Research and Development Technical Report

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INVESTIGATIONS OF THE SAFETY OF Li/SOC1$_2$ BATTERIES

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Forced overdischarge behavior of Li/SOCl$_2$ cells was studied using spirally wound C-size and small prismatic cells. Cathode and anode limited cells were tested. Cathode limited cells could be overdischarged for long periods of time without explosions.

Anode limited cells are potentially hazardous. One out of three cells overdischarged at 100 mA exploded.

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Electrolyte from overdischarged cells was analyzed. SO_2Cl_2 and $SOCl^+ AlCl_4^-$ were identified as products. These solutions also contain a material with an IR absorption at 1070 cm^{-1} which has not yet been characterized.

The charging behavior of $Li/SOCl_2$ cells was also investigated. A charging current can be applied to either new or partially discharged cells without apparent hazard. No net changes appear to occur in the cells upon extensive "charging" suggesting a sequence of regenerative reaction.

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I. INTRODUCTION

In recent years there has been considerable research and development on ambient temperature, high energy density Li cells. A particularly promising system is based on $SOCl_2$ (1,2). Here, $SOCl_2$ serves as both a solvent and depolarizer for the cell. These cells have delivered 100 Whr/lb and 40 W/lb at the 2.5-hour rate and, as usual, higher energy densities at lower discharge rates (3). According to one report (4) they can deliver as much as 300 Whr/lb at low rates. Clearly this is a very promising system with many applications where high energy density and high rate are required.

The cell has two problems: (1) under a variety of circumstances, the cell has shown a tendency to explode, (2) after high temperature storage, it shows voltage delay.

The objective of this program is to explore the causes and find solutions to the explosion hazards in the $Li/SOCl_2$ cells. Three types of explosion have been reported: (1) cells explode on short circuit; (2) cells explode on forced overdischarge; (3) cells explode on resistive load overdischarge. Clearly, any high rate, high energy density system such as $Li/SOCl_2$ has the possibility of a thermal runaway type of explosion. It is not surprising that a hermetically sealed D-cell, which can deliver in excess of 20 amps, might explode when short circuited -- it just is not possible to remove the waste heat. However, this problem appears to have been solved with low pressure vents (100-300 psi) and with appropriate fuses incorporated into the cell (5,6).

The other two types of explosion are of greater concern. The forced overdischarge situation may be experienced by a cell in a battery package. Explosion on resistive load overdischarge implies that any completely discharged cell still connected to a piece of equipment is a hazard. No clear documentation of the explosion hazard on resistive load overdischarge is found in the literature. Forced overdischarge explosions have been documented for D-size (5) and C-size (7,8) $Li/SOCl_2$ cells. This type of explosion, occurring after cell-voltage reversal, takes place without prior temperature or pressure rise and appears to be chemical in its origin. We have shown that forced overdischarge explosions appear to occur only in anode limited cells (7,8). Individual electrode potential measurements during discharge and overdischarge showed that the anode was at $\geq 4.0V$ for a considerable length of time prior to an explosion. The nature of the explosion suggests the production of sensitive chemicals by oxidation of $SOCl_2$ or other materials present in the cell which could explode under certain conditions. Several questions remain to be answered. They include (1) what is the effect of current density?

1

(2) What roles do cell geometry and cell size play? (3) What is the role of the supporting electrolyte? (4) What is the explosive material? (5) What initiates the explosion and what is the mechanism of propagation?

During the first quarter of the present contract, our work centered on defining more clearly the above questions. We have also examined, briefly, the behavior of $Li/SOCl_2$ cells on charging.

II. FORCED OVERDISCHARGE BEHAVIOR OF Li/SOCl$_2$ CELLS

1.   C-Size Cells

C-size Li/SOCl$_2$ cells with spirally wound electrodes were constructed and specially instrumented for measuring individual electrode potentials and temperature. Special emphasis was placed on the configuration of these cells, i.e., whether they were cathode or anode limited.

1.1 Experimental Procedures

All the experiments involving reagent handling and cell construction were carried out in the absence of air and moisture in an argon atmosphere using a Vacuum-Atmospheres Corporation dry box. Discharges and overdischarges of sealed cells were carried out galvanostatically after enclosing them in steel containers capable of withstanding the force of an eventual explosion.

  ● Cell Construction

C-cells were constructed using the typical parameters given below:

C Cathode: 10" × 1.5"; 0.024" thick. The cathode contained 1.70 ± 0.2g of the cathode mix, comprising 85% Shawinigan carbon and 15% Teflon, bonded on expanded Ni, 5Ni5-5/0.

Li Anode: 10" × 1.5"; 0.017" thick Li foil pressed on expanded Ni, 5Ni7-4/0.

In some cells, electrode parameters varied slightly from those given above. These are appropriately indicated in the text.

Separator: 2" × 11.5"; 0.005" thick, all-glass filter paper containing 4% PVA binder (Mead Paper Specialty, Catalog No. 934-S).

Electrolyte: 12 ml 1.8M LiAlCl$_4$/SOCl$_2$. The electrolyte was prepared as described below.

Cell Containers: Stainless steel (No. 316) can; height = 2.1", OD = 1.00".

The Li anode, the carbon cathode and the glass filter paper separator were wound into a tight roll such that the Li formed the outer layer of the roll. The roll was then introduced into the can which contained two layers of the 5 mil thick separator at the bottom as an insulator. The cap served as the negative terminal. The cell top consisted of a stainless steel plate with a Viton rubber gasket. The cell top was held tightly in place by threaded steel bolts leading to a bottom plate. Compression springs were used and adjusted such as to allow cell venting above a pressure of 120 psi. The positive lead connection was made through a Conax feedthrough attached to the top of the steel plate. A reference electrode, consisting of a piece of Li foil attached to a nickel wire, was positioned on top of the cell package before sealing the cell. The reference electrode lead was also taken through the Conax fitting. Temperature measurements were made with a copper-constantan thermocouple junction placed either on the cell wall or at the center of the electrode package. In the latter case it was introduced into the cell package through the Conax fitting. It was electrically insulated by Teflon tape or Teflon shrink tube. A schematic of a fully sealed cell is shown in Figure 1.

- ### Electrolyte Preparation

Experiments were carried out using $LiAlCl_4$ and $Li_2O/AlCl_3$ based electrolytes. Lithium tetrachloroaluminate, $LiAlCl_4$, was initially synthesized as the melt and purified by electrolysis. In this preparation, 1 mol of LiCl (Fisher L-121), which was predried in vacuum (10^{-3} torr) at 400°C for $\sim$4 hr, and 1 mol of $AlCl_3$ (Fluka, puriss) were melted together in a Pyrex container. The temperature was maintained at $\sim$190°C. The product was light yellow. The melt was purified by anodizing a piece of pure Al (Ventron m5N ingot) against an Al wire cathode. The anodization was continued for $\sim$24 hr at 4 mA/cm^2 (40 mA). At the end of electrolysis, the melt was water white. The cooled melt was powdered with a mortar and pestle. The $LiAlCl_4/SOCl_2$ electrolyte of appropriate concentration was prepared by dissolving the salt in $SOCl_2$ (Eastman Kodak, Catalog No. 246) at room temperature.

The electrolyte based on $Li_2O/AlCl_3$ (9) was prepared by stirring Li_2O (ROC/RIC) with a solution of $AlCl_3$ in $SOCl_2$ at room temperature for more than 48 hr. To ensure complete conversion of $AlCl_3$ into ionic species, the Li_2O and $AlCl_3$ were originally mixed in the ratio 1.25:2. The reaction was followed by IR spectrometry (Figure 2). At the end, the unreacted Li_2O was filtered off.

1.2 Results and Discussion

1.2.1 Cathode Limited Cells

In a cathode limited cell, the end of cell life is caused either by blockage of the carbon current collector by discharge products or by depletion

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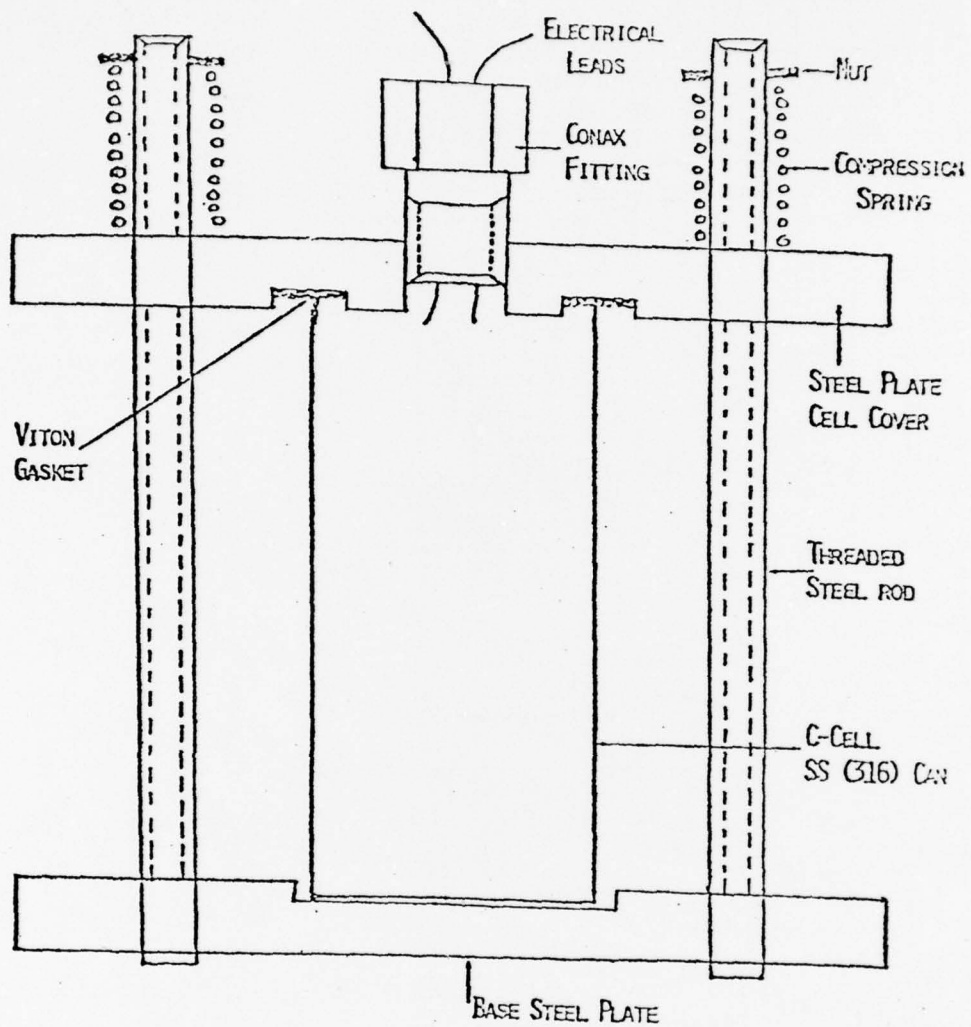VITON
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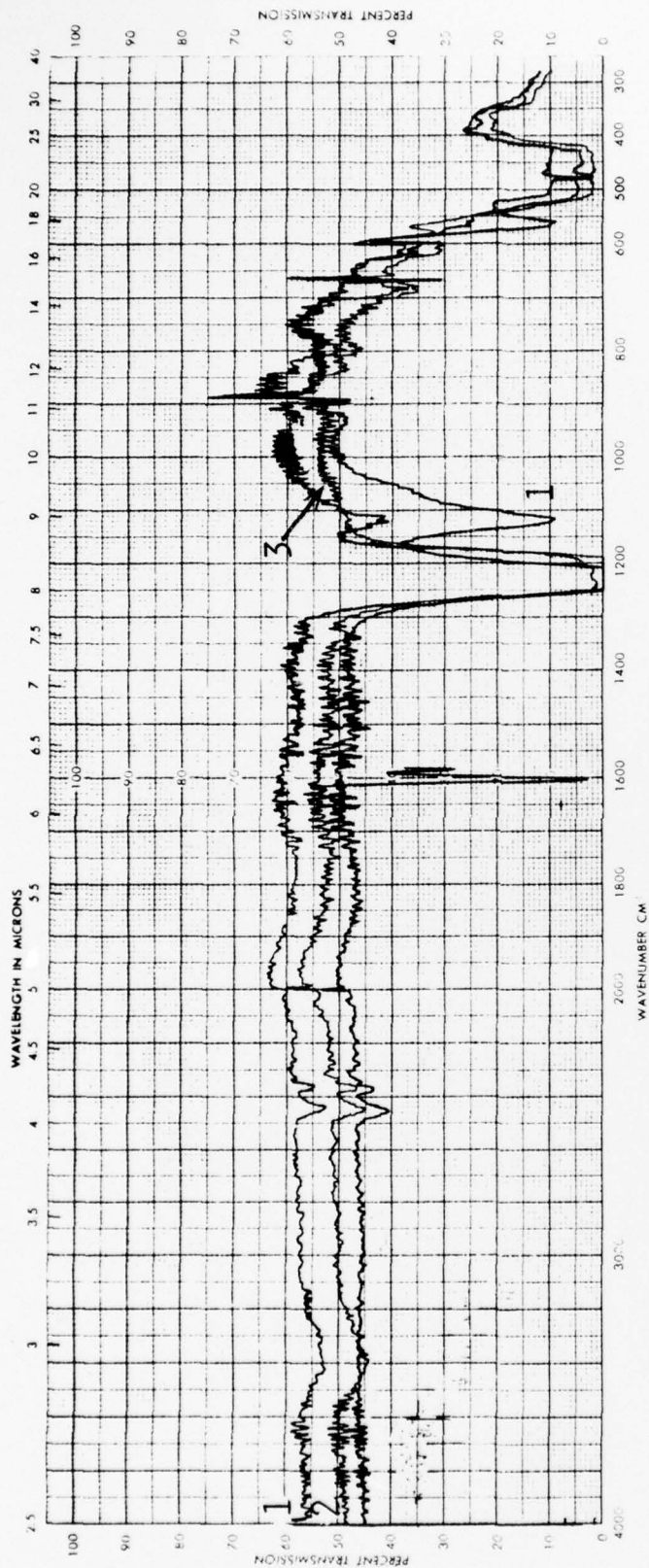SS (316) CAN

BASE STEEL PLATE

Fig. 1. A schematic view of an assembled Li/SOCl$_2$ C-cell.

Fig. 2. Infrared spectrum of SOCl2/1M AlCl3 solution as a function of added Li2O. (1) SOCl2/1M AlCl3 solution; (2) SOCl2/1M AlCl3 solution with 0.5M Li2O stirred for >48 hr; (3) SOCl2/1M AlCl3 with 0.7M Li2O stirred for >48 hr.

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of the $SOCl_2$ depolarizer. In either event, at the end of discharge the cathode potential changes towards and on overdischarge beyond the Li electrode potential. During forced overdischarge, Li is plated onto and into the carbon resulting in very small cell voltages, ~100 mV. Detailed parameters of the various cells tested are shown in Table 1.

Cell C-7 was built with the thermocouple junction placed inside the cell at the center of the electrode package. The junction was situated at about the half-way mark of the full length of the electrode package. The cell was discharged and overdischarged at 100 mA (0.66 mA/cm^2 of Li electrode area). Voltage/time plots of the cell potential and the potential of the Li-anode vs. a Li reference electrode and a plot of temperature vs. time are shown in Figure 3. The discharge capacity of 4.2 Ah to zero volt corresponds to a cathode utilization of 2.74 Ah/g carbon and suggests that the end of cell life occurred due to cathode blockage. The anode potential remained close to zero volt during most of the discharge. However, towards the end of discharge, as the cell voltage approached zero, there was a temporary polarization of the anode to more positive potentials. This temporary anode polarization probably reflects the inhomogeneous current distribution at the end of the useful carbon electrode life resulting in high local current densities at the Li electrode. The average current density corresponding to the 100 mA discharge was 0.66 mA/cm^2. The high overvoltages at both electrodes in this transition region also result in increased heat generation leading to a temperature peak. The cell was overdischarged also at 100 mA. The cell did not explode even after 10.5 Ah of overdischarge. The total charge passed through the cell now was 15 Ah. The amount of Li and $SOCl_2$ originally present was 8.18 Ah and 7.4 Ah respectively.

Cell C-2 was tested at 200 mA (1.32 mA/cm^2 of Li electrode area). Its behavior during discharge and overdischarge (Figure 4) is similar to that of cell C-7. The cell yielded 3.5 Ah capacity, equivalent to a cathode utilization of 2.23 Ah/g carbon. The cell did not explode even after 25 Ah of overdischarge. The results agree with our previous observation that cathode limited cells can be forced overdischarged for long periods of time without apparent problems. Furthermore, the data shows that the internal cell temperature remains close to ambient both during discharge and overdischarge.

- ## Post-Test Examination of Cathode Limited Cells

Post-test examination revealed that in all cathode limited cells, inspite of the long periods of overdischarge, some Li remained on the anode. This and the low Li electrode polarization strongly support short circuiting due to Li dendrites. Thus, during overdischarge the majority of the current does not result in plating of Li onto the cathode.

TABLE 1

CELL PARAMETERS FOR CATHODE-LIMITED Li/SOCl$_2$ C-CELLS

Cell No.	Carbon Electrode			Lithium Electrode		Electrolyte SOCl$_2$/1.8M LiAlCl$_4$		Discharge Current (mA)
	Average Thickness (mm)	Total Area (cm^2)	Amount of Carbon (g)	Total Area* (cm^2)	Amount of Li (Ah)	Vol. (ml)	Capacity (Ah)	
C-7	0.66	184	1.53	152	8.18	12	7.4	100
C-2	0.66	184	1.57	160	6.3	12	7.4	200

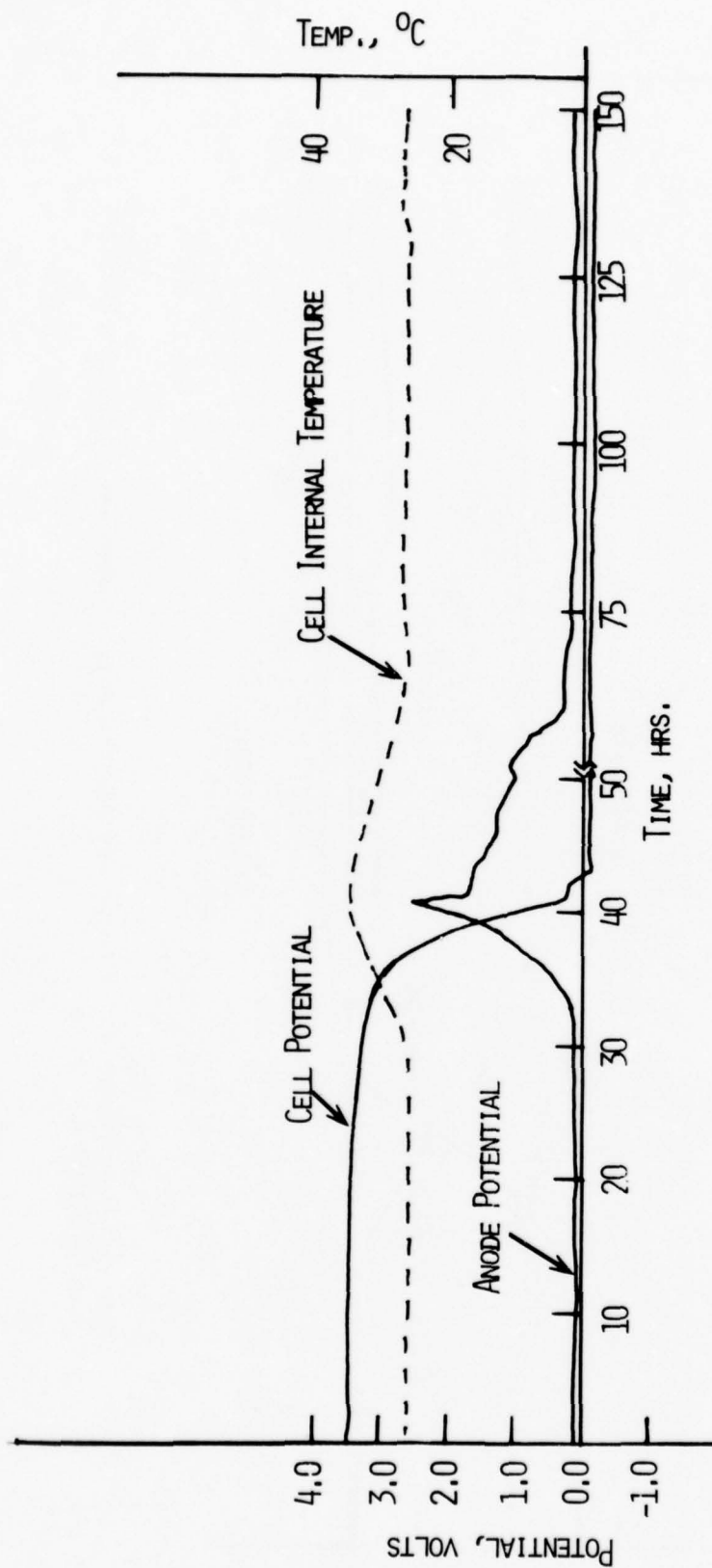*Area corrected for Li not facing carbon cathode.

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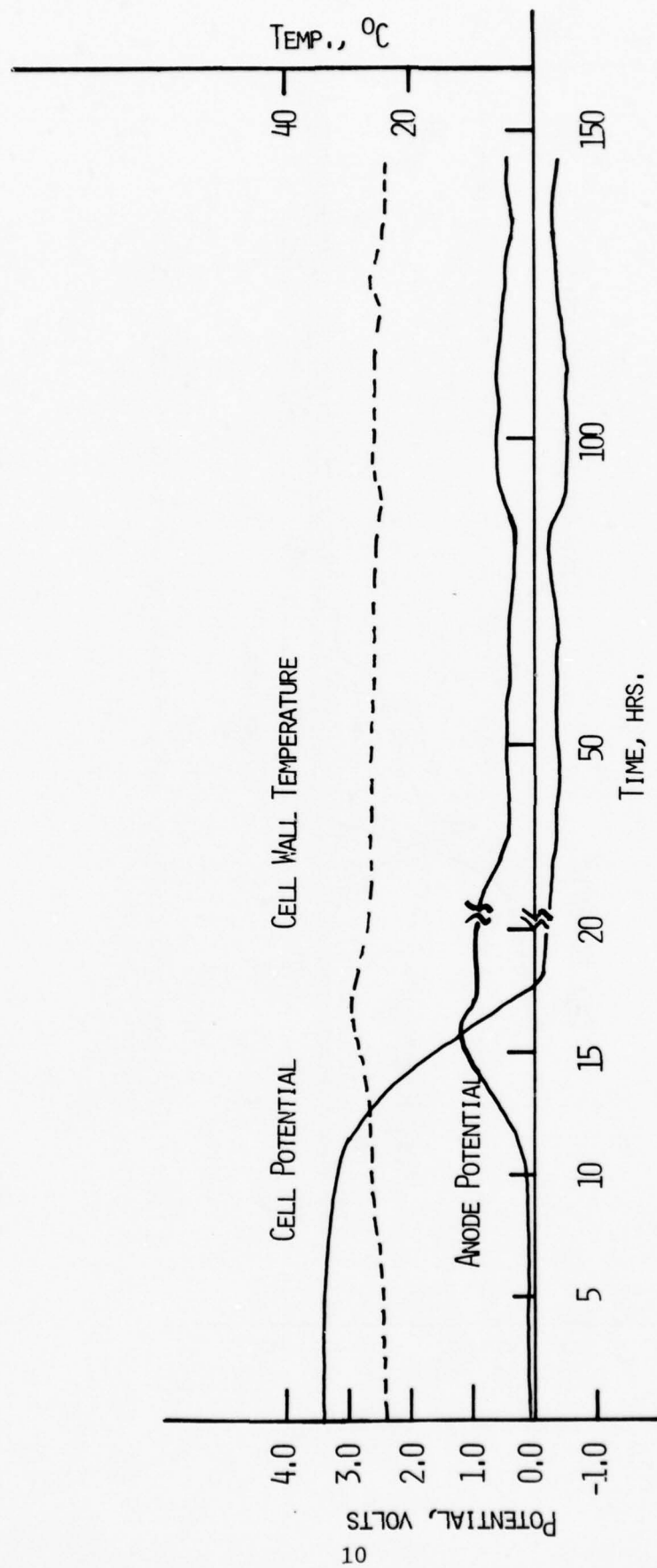Fig. 3. Galvanostatic discharge and overdischarge curves for Li/SOCl$_2$ cell C-7. Current = 100 mA.

Fig. 4. Galvanostatic discharge and overdischarge curves for Li/SOCl$_2$ cell C-2. Current = 200 mA.

The carbon cathodes in these cells have become very brittle and easily breakable. The electrode surface is covered, often non-uniformly, with discharge products, predominantly LiCl. Cathodes from cells which have been overdischarged for long periods of time have consistently shown extreme moisture sensitivity, often catching fire in contact with water. The handling and disposal of cathodes from overdischarged cathode limited cells requires special care. The fire hazard of the cathode may be due to the high surface area of Li plated onto it during overdischarge. It is also possible that the majority of the plated Li is present as an intercalate of carbon (10) and the form may be more sensitive (less easily passivated) than Li foil itself.

1.2.2 Anode Limited Cells

In anode limited cells, the end of cell life is determined by Li electrode polarization. This can be either due to Li depletion or due to loss of contact between Li and the Exmet grid. Cell C-1 was discharged and overdischarged at 100 mA (0.64 mA/cm^2 of Li electrode area). The cell parameters are given in Table 2. The cell, shown in Figure 5, gave a capacity of only 2.5 Ah, although the amount of Li originally present was 6.1 Ah. It appears that the Li electrode prematurely polarized due to loss of contact of Li with Exmet grid. The Li was pressed onto the grid at a pressure less than 50 psi. It may be noted that towards the end of discharge the cell voltage showed fluctuations which were also reflected in the anode potentials. It appears that the voltage fluctuations are related to the breaking and making of contact of the Li foil with the anode Exmet grid. The cell was overdischarged also at 100 mA. The fluctuations of the anode potential continued during overdischarge reaching occasionally ∿8V vs. Li$^+$/Li. The cell exploded at the 126th hr of test. The temperature, measured here at the external cell wall, increased sharply. There was no gradual increase in temperature prior to the explosion. In fact the temperature decreased for several hours prior to the explosion as a result of reduced cell polarization. The cell vent opened as a result of the explosion. We found fused metal at the mouth of the nickel can where this venting occurred indicating that the materials which escaped during the venting were extremely hot. Post-test examination revealed that the explosion damage was almost exclusively confined to the anode. Large areas of the anode grid were missing whereas the cathode remained intact. The explosion occurred in only the part of the cell opposite to the location of the thermocouple. This accounts probably for the relatively low peak temperature measured. The local temperatures in the cell must have been much higher than this. The general character of this explosion closely resembled our earlier observations (7,8). However, this was the first time we encountered an explosion upon overdischarge of a C-cell at 100 mA. All previous explosions occurred at 50 mA. Explosions appear to occur at random. Other apparently identical test cells did not explode.

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TABLE 2

CELL PARAMETERS FOR ANODE-LIMITED Li/SOCl$_2$ C-CELLS

Cell No.	Carbon Electrode			Lithium Electrode		Electrolyte SOCl$_2$/1.8M LiAlCl$_4$		Discharge Current (mA)
	Average Thickness (mm)	Total Area (cm^2)	Amount of Carbon (g)	Total Area* (cm^2)	Amount of Li (Ah)	Vol. (ml)	Capacity (Ah)	
C-1	0.72	184	1.60	156	6.1	12	7.4	100
C-3	0.66	189	1.60	156	6.1	12	7.4	200
C-6	0.67	179	1.58	161	6.3	12	7.4	100

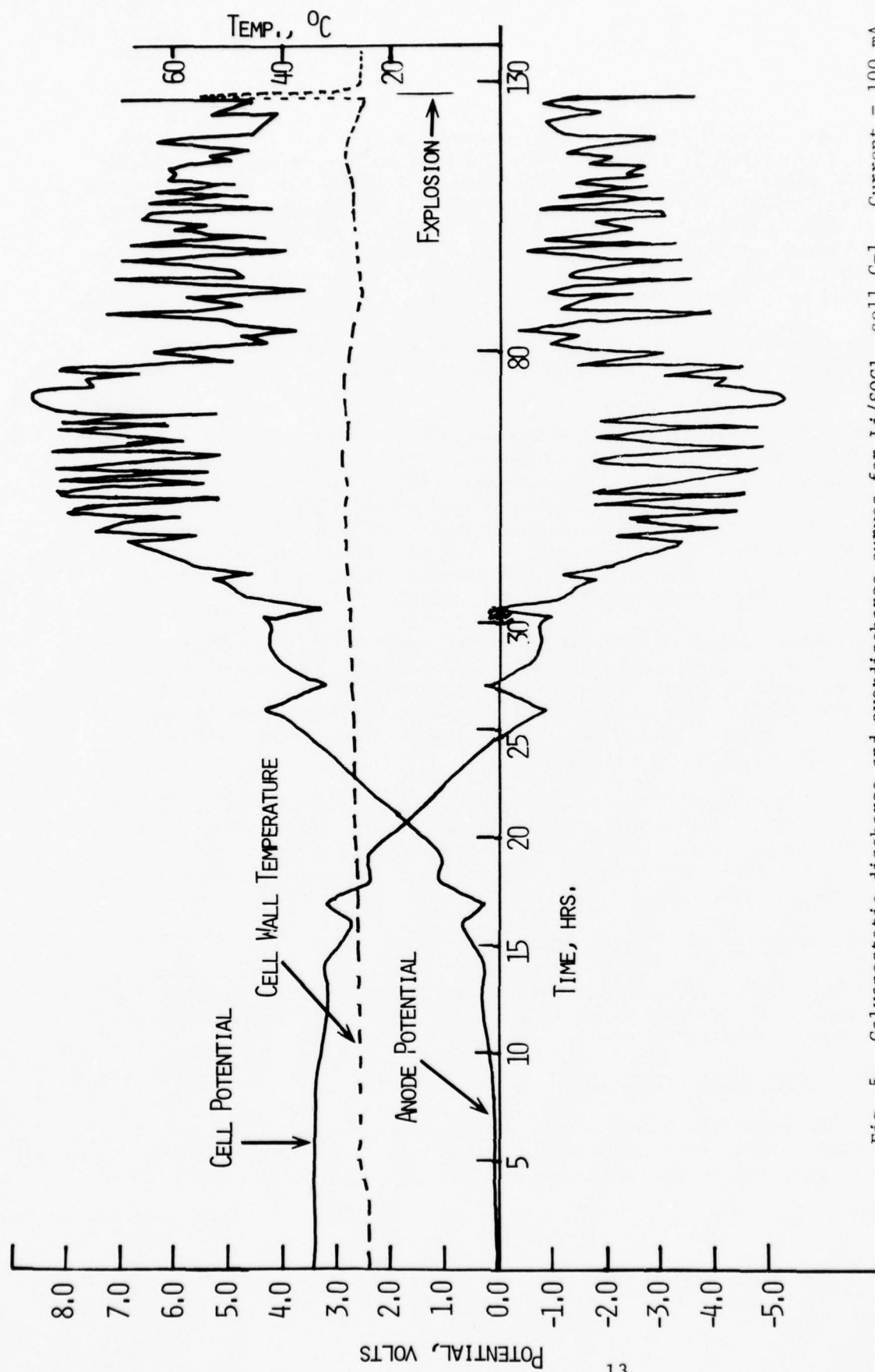*Area corrected for Li not facing carbon cathode.

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Fig. 5. Galvanostatic discharge and overdischarge curves for Li/SOCl$_2$ cell C-1. Current = 100 mA.

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The test results of cell C-3 are shown in Figure 6. The parameters for cell C-3 are given in Table 2. The cell was discharged at 200 mA (1.26 mA/cm^2 of Li electrode area). The cell capacity to zero volt was 3.5 Ah which was equivalent to a cathode capacity of 2.18 Ah/g carbon. As observed previously for cell C-1, the anode potential showed fluctuations during the end of discharge and during overdischarge. Although the cell was overdischarged for 122.5 hr (24.5 Ah) it did not explode. It may be noted that the cell wall temperature remained close to ambient during the entire test.

Post-test examination revealed that some Li remained on the anode; but it was present in small pieces distributed in different parts of the Exmet grid.

The cell parameters of cell C-6 are given in Table 2 and the discharge and overdischarge are depicted in Figure 7. In this cell temperature was monitored with an internal thermocouple as in the cathode limited cell discussed earlier. The cell was discharged and overdischarged at 100 mA (0.62 mA/cm^2 of Li electrode area). During the discharge the temperature remained close to that of the ambient. As the cell potential approached zero volt at the end of discharge the temperature gradually increased to ∿36°C and during overdischage it stabilized at 30°C.

The average internal temperature during overdischarge is slightly higher than what was observed in the cathode limited cell tested earlier. It is interesting that after ∿68 hr of test the anode potential gradually decreased and stabilized at values close to the Li potential resembling the behavior of cathode limited cell. During this part of the overdischarge the temperature was close to the ambient.

Although the average internal temperature in anode limited cells during overdischarge is slightly higher than in cathode limited cells, it is not significantly different. The higher temperature is a reflection of the different reactions occurring in anode limited cells when the anode potentials are at values greater than 4V.

2.   Small Prismatic Li/SOCl$_2$ Cells

The forced overdischarge behavior of small prismatic Li/SOCl$_2$ cells, which are about 1/5 the size of the C cells, was studied in both the cathode and anode limited configurations.

2.1 Experimental Procedures

The prismatic Li/SOCl$_2$ cell comprised an electrode package assembled with alternating carbon and Li electrodes, each separated by a 5 mil fiber glass separator. A schematic of the electrode arrangement is
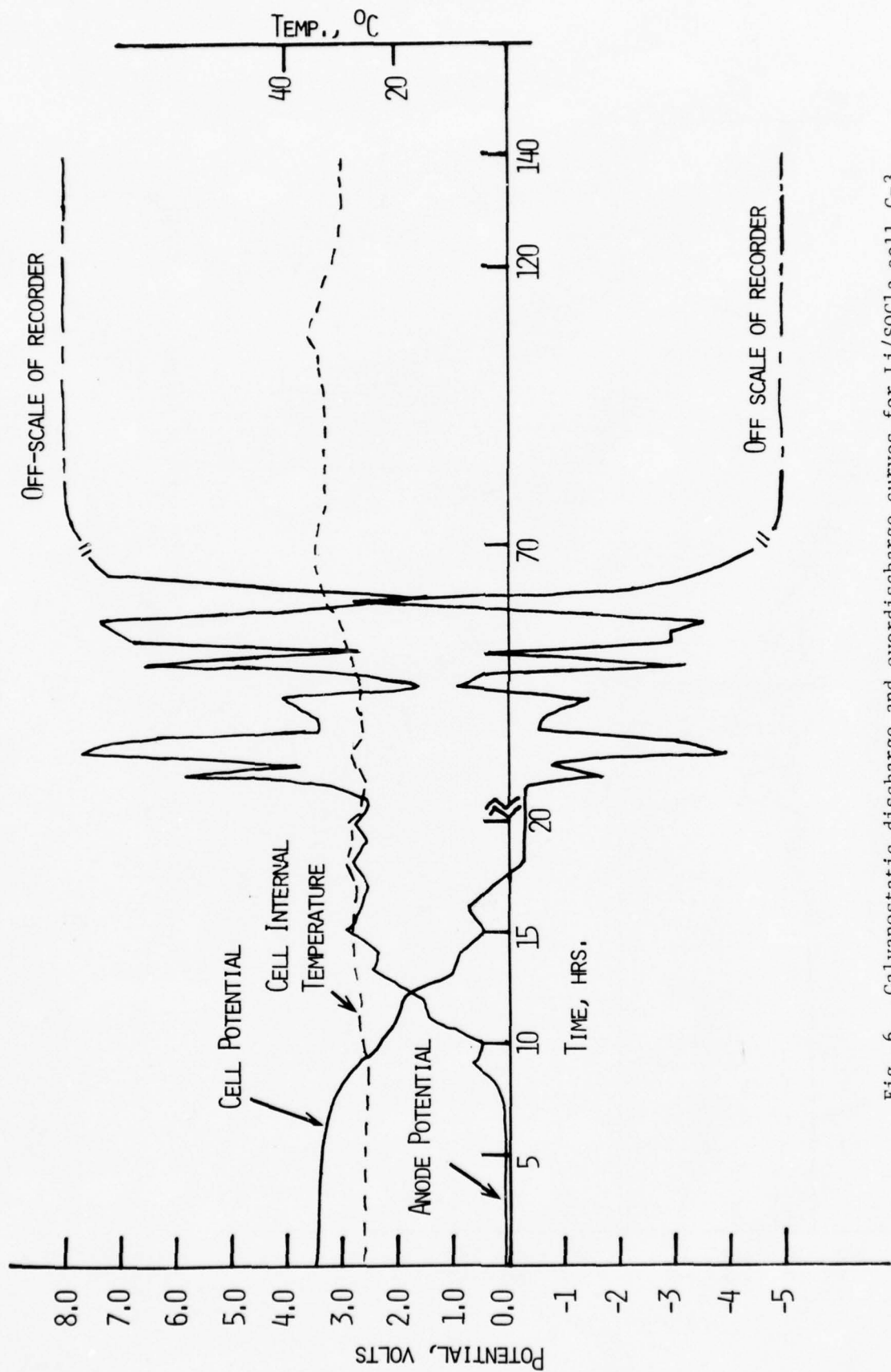
Fig. 6. Galvanostatic discharge and overdischarge curves for Li/SOCl2 cell C-3. Current = 200 mA.
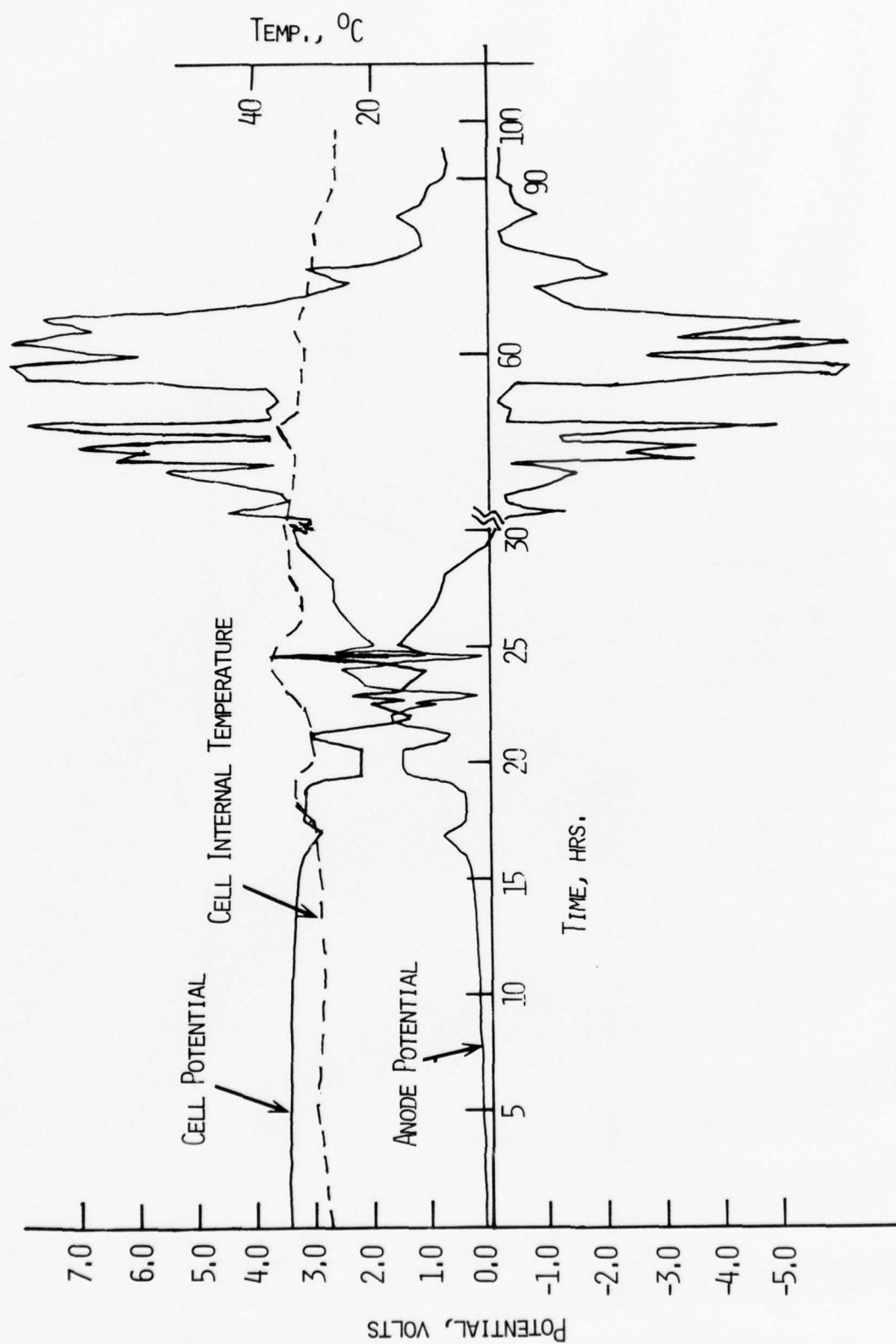
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Fig. 7. Galvanostatic discharge and overdischarge curves for Li/SOCl$_2$ cell C-6. Current = 100 mA.

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is shown in Figure 8. The package was introduced into a rectangular glass vial, $0.8 \times 2.4 \times 4.0$ cm and the glass vial was tightly closed with rectangular coverplates in a manner similar to that in the C-cells. Except for the rectangular shape, the cell assembly resembles that of the C-cell shown in Figure 1. The electrode connections were m e through the Conax fitting on the coverplate. A Li reference electrode was also placed in each cell.

2.2 Results and Discussion

The various cells tested and their construction parameters are shown in Table 3. Cell P-4, shown in Figure 9, is a cathode limited cell as evidenced by the Li electrode potentials which remained close to zero during discharge and overdischarge. A temporary anode polarization at the end of discharge was observed as in the case of the C-cells. The discharge current of 36 mA corresponded to a current density of 1 mA/cm^2 after electrode area. The discharge capacity of 880 mAh was equivalent to a cathode utilization of 2.82 Ah/g carbon which is similar to that found in the C-cells. The cell was overdischarged for 120 hr (4.32 Ah) without explosion. The total charge passed would be equivalent to $>5e^-/SOCl_2$. The result indicates that short circuit occurs in forced overdischarge of prismatic $Li/SOCl_2$ as observed in spirally wound cells. Forced overdischarge behavior of anode limited prismatic cells, P-5 and P-8 were also tested. The parameters for these cells are shown in Table 3.

Cell P-5, depicted in Figure 10, gave a capacity of 470 mAh. The discharge was limited by Li depletion. The cathode utilization was equivalent to 2.2 Ah/g carbon. The overdischarge proceeded with considerable fluctuations in anode potentials reaching values as high as 9.0V. The behavior is similar to that found in C-cells. The cell did not explode although it was overdischarged for 70 hr (1.68 Ah).

In cell P-8, shown in Figure 11, an amount of electrolyte lower than present in cell P-5 was used. The forced overdischarge behavior is similar to that of cell No. 5. The cell did not explode even after overdischarge for 65 hr (1.6 Ah).

Cell P-18, shown in Figure 12 and tested in the flooded configuration also behaved similar to cells P-5 and P-8. It also exhibited safe behavior inspite of the long period of forced overdischarge.

In summary, none of the anode limited small prismatic cells tested exploded. It appears that special conditions are required to bring about an explosion. More tests with variations of all parameters including $LiAlCl_4$ concentration, $SOCl_2$ to carbon ratio and current density will have to be conducted.
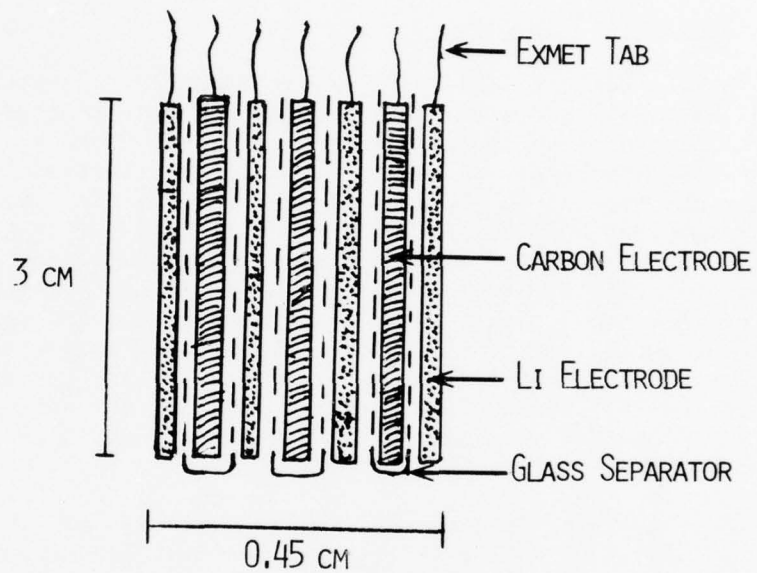
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Fig. 8. A typical arrangement of electrodes in a prismatic cell.

TABLE 3

CELL PARAMETERS FOR SMALL PRISMATIC CELLS

Cell No.	Cell Configuration	Carbon Electrode Average Thickness (mm)	Carbon Electrode Total Area Facing Li (cm^2)	Carbon Electrode Approximate Amount of Carbon (mg)	Lithium Electrode Area (cm^2)	Lithium Electrode Amount (Ah)	Electrolyte LiAlCl$_4$/SOCl$_2$ Con. LiAlCl$_4$ (M)	Electrolyte LiAlCl$_4$/SOCl$_2$ Vol. (ml)	Electrolyte LiAlCl$_4$/SOCl$_2$ Capacity (Ah)	Discharge Current (mA)
P-4	Li/C/Li/C/Li/C/Li (cathode limited)	0.61	36	320	36	2.01	1.8	3	1.84	36
P-5	C/Li/C/Li/C (anode limited)	0.61	24	320	24	0.70	1.8	3	1.84	24
P-8	C/Li/C/Li/C (anode limited)	0.68	24	420	24	0.70	1.8	2	1.23	24
P-18	C/Li/C/Li/C (anode limited)	0.65	24		24	0.70	1.8	4.5*	–	24
P-15	Cathode limited	0.70	36	450	36	2.01	1.00**	3	1.84	36

*This cell utilized a "flooded configuration" so that the electrolyte could be directly analyzed by IR.
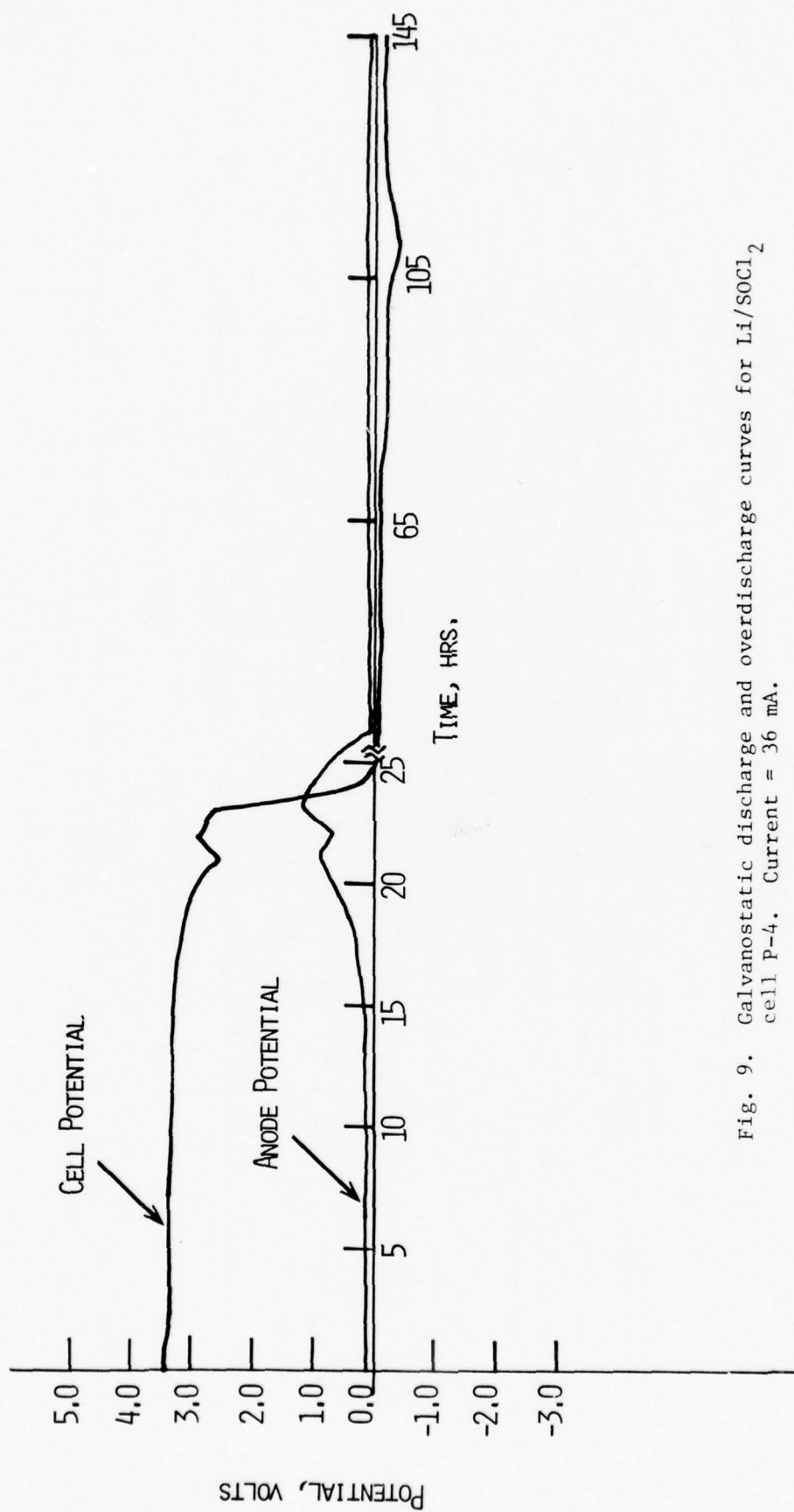**Li$_2$O/AlCl$_3$ based electrolyte.

Fig. 9. Galvanostatic discharge and overdischarge curves for Li/SOCl$_2$ cell P-4. Current = 36 mA.
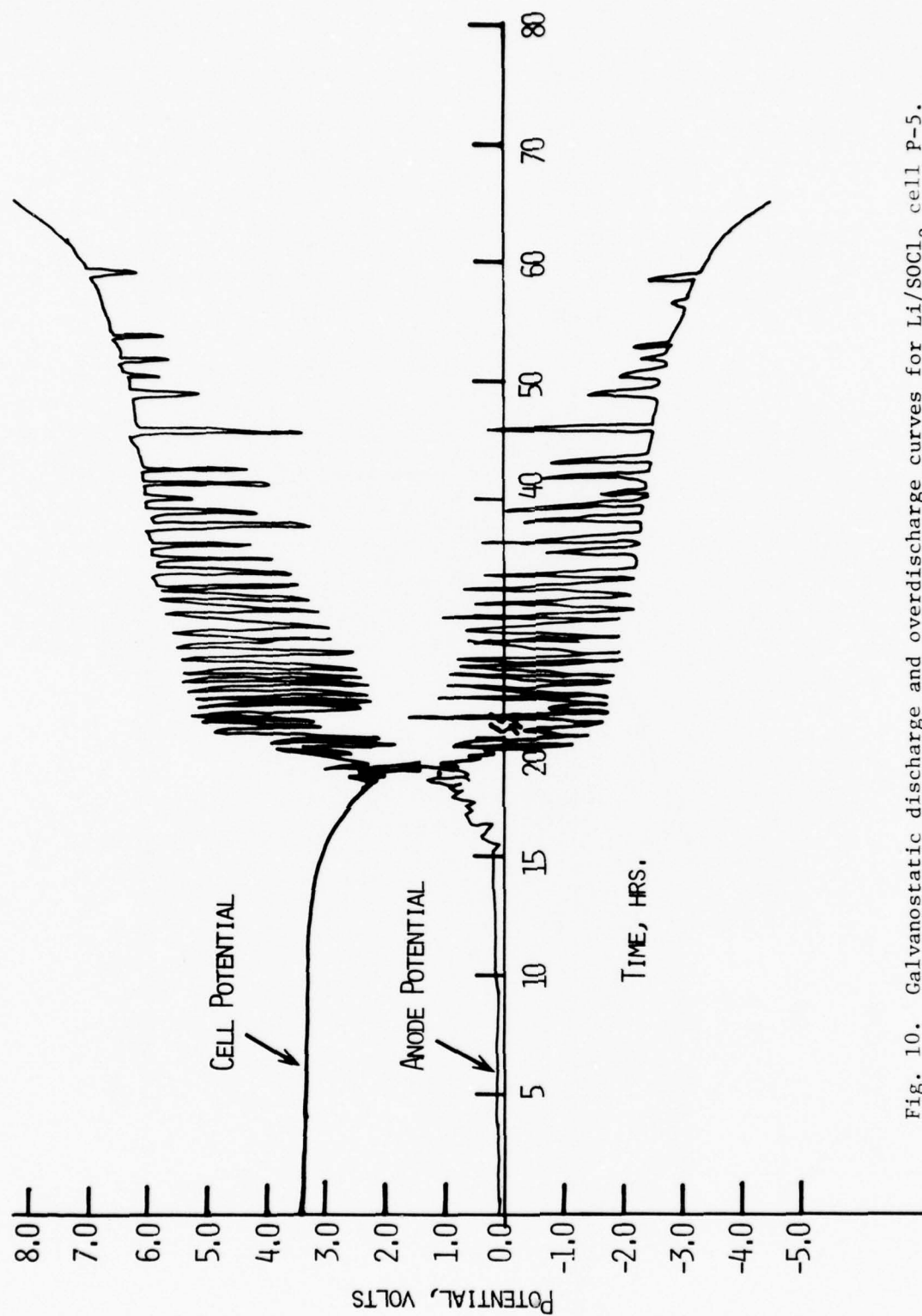
20

Fig. 10. Galvanostatic discharge and overdischarge curves for Li/SOCl$_2$ cell P-5. Current = 24 mA.
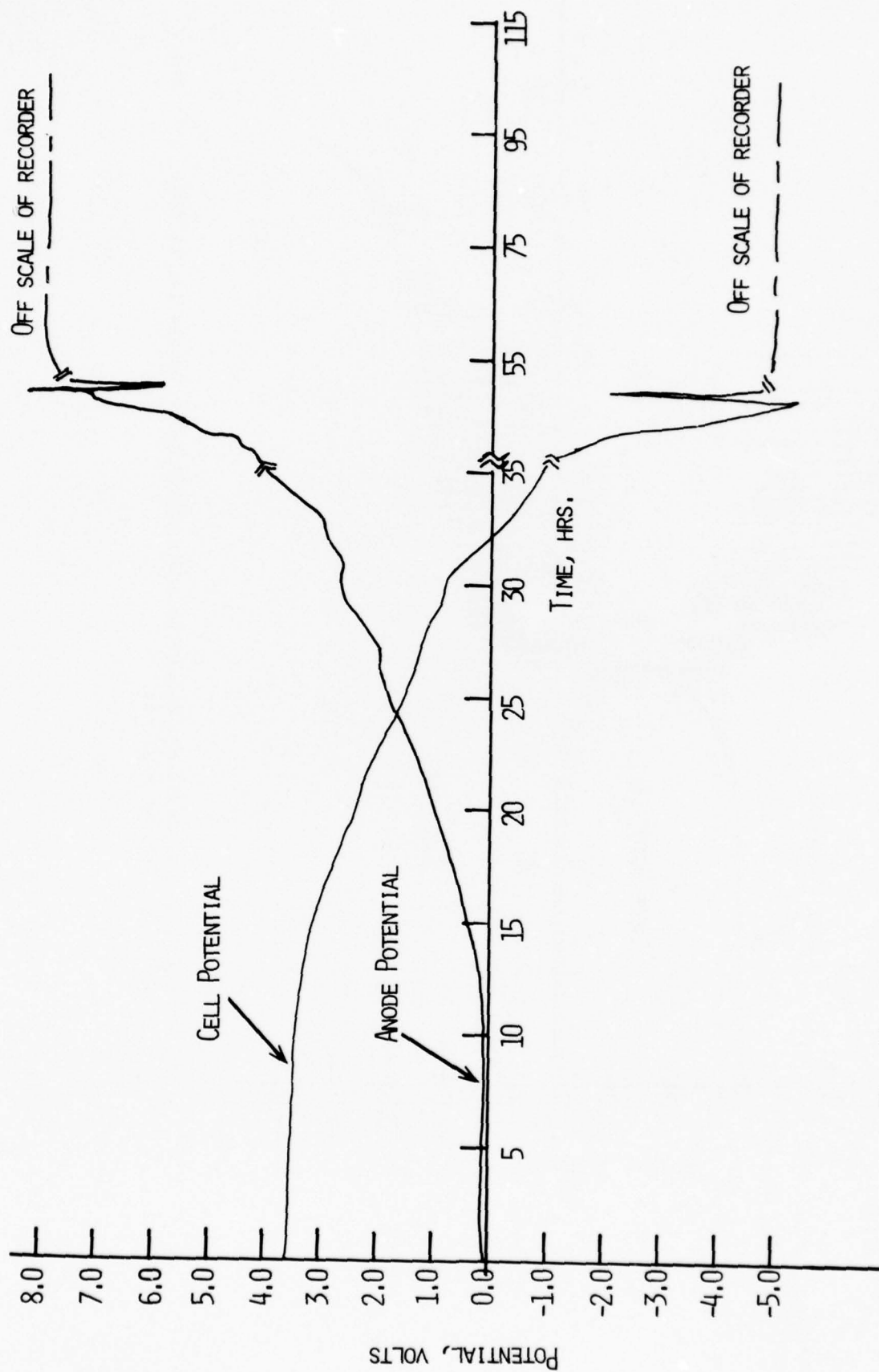
21

Fig. 11. Galvanostatic discharge and overdischarge curves for Li/SOCl$_2$ cell P-8.
Current = 12 mA.

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3.   Analytical Studies

A most important step in understanding the chemistry of $Li/SOCl_2$ cells and in avoiding potentially hazardous conditions is to identify the various reaction products. During this quarter an attempt was to identify reaction products by IR spectrometry* from $Li/SOCl_2$ cells after forced overdischarge.

3.1   Analysis of the $SOCl_2$- or S_2Cl_2-Extract from Overdischarged $Li/SOCl_2$ Cells

Two anode limited cells, P-5 and C-6 after the overdischarge shown in Figures 10 and 7 respectively, were carefully disassembled in the drybox and the electrode package was extracted with $SOCl_2$. The spectrum of the extract from C-6 is shown in Figure 13. The spectrum shows the presence of $SOCl_2$ (1230 cm^{-1}, V_1, S-O symmetric stretch) and SO_2 (1335 cm^{-1}, V_3, S-O asymmetric stretch. There is a new peak at 1070 cm^{-1}, not present either in $SOCl_2$ or in $SOCl_2/LiAlCl_4$. However, the peak at 1070 cm^{-1} has been previously observed in the $SOCl_2/LiAlCl_4$ electrolyte which had been stored at 70°C in contact with Li (11). The nature of the compound giving rise to this absorption has not been identified. The identical spectrum (see Fig. 13) was obtained from the extract from P-5, the anode limited prismatic cell.

In order to examine the potential presence of new materials, masked by the strongly absorbing $SOCl_2$ peak at 1230 cm^{-1}, the overdischarged prismatic cell P-8, shown in Figure 11, was extracted with S_2Cl_2** and the spectrum of the extract was recorded. The spectrum was identical to those from P-5 and C-6.

The only product identifiable in the vapor phase infrared spectrum of volatile materials from an anode limited C-cell during various stages of overdischarge was SO_2.

3.2   Direct Analysis of the Electrolyte from Overdischarged $Li/SOCl_2$ Cells

In order to minimize any degradation of unstable compounds formed during forced overdischarge, IR spectra were recorded of the electrolyte

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*All spectra were obtained on a Beckman Acculab 5 dual beam spectrometer. The instrument covers the range from 4000 cm^{-1} to 375 cm^{-1}. All the liquid spectra were obtained with Beckman TAC cells. These have AgCl windows of 0.025 to 0.1 mm path length and can be sealed permanently.

**The S-Cl bonds absorb below 600 cm^{-1}.
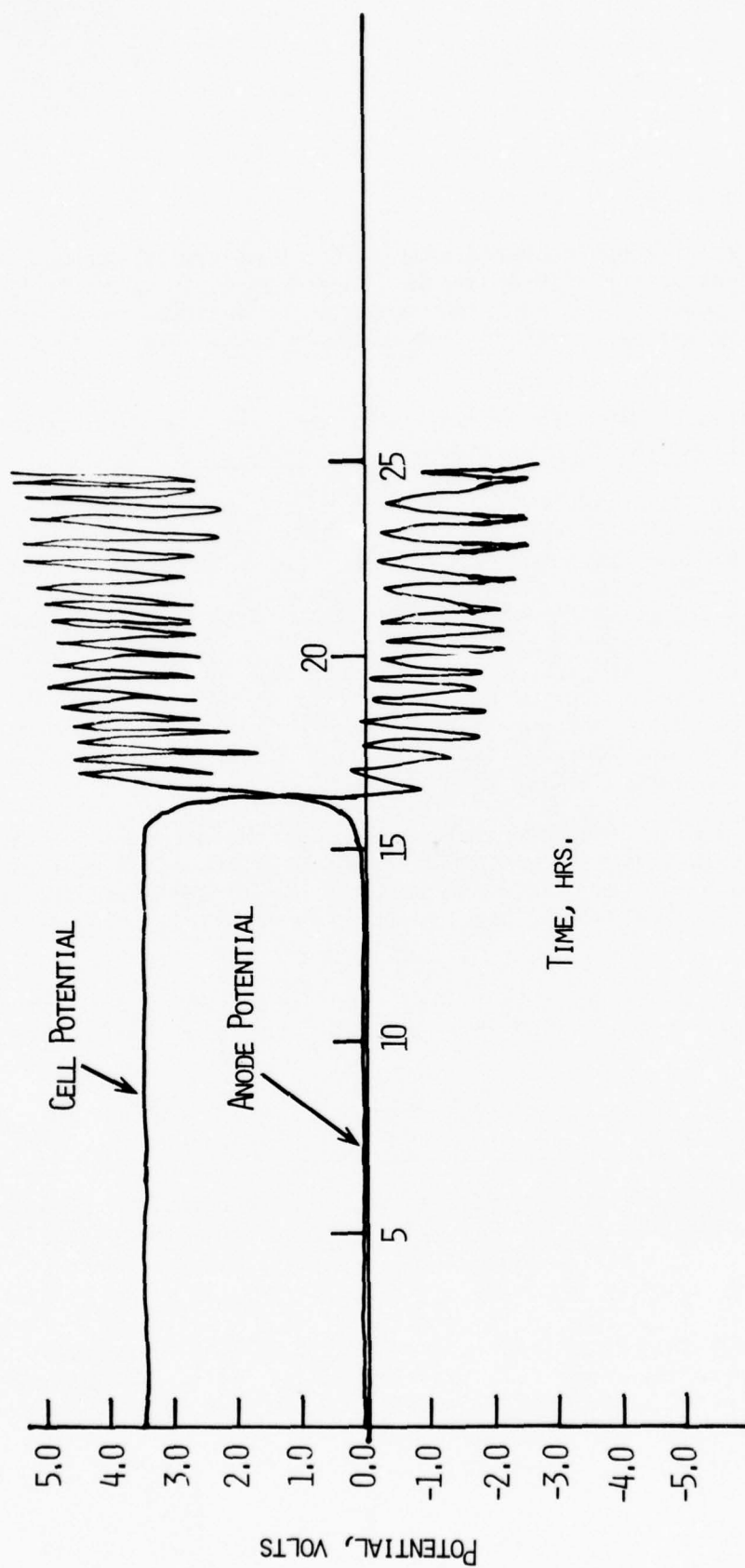
Fig. 12. Galvanostatic discharge and overdischarge curves for Li/SOCl$_2$ cell P-18. Current = 24 mA.
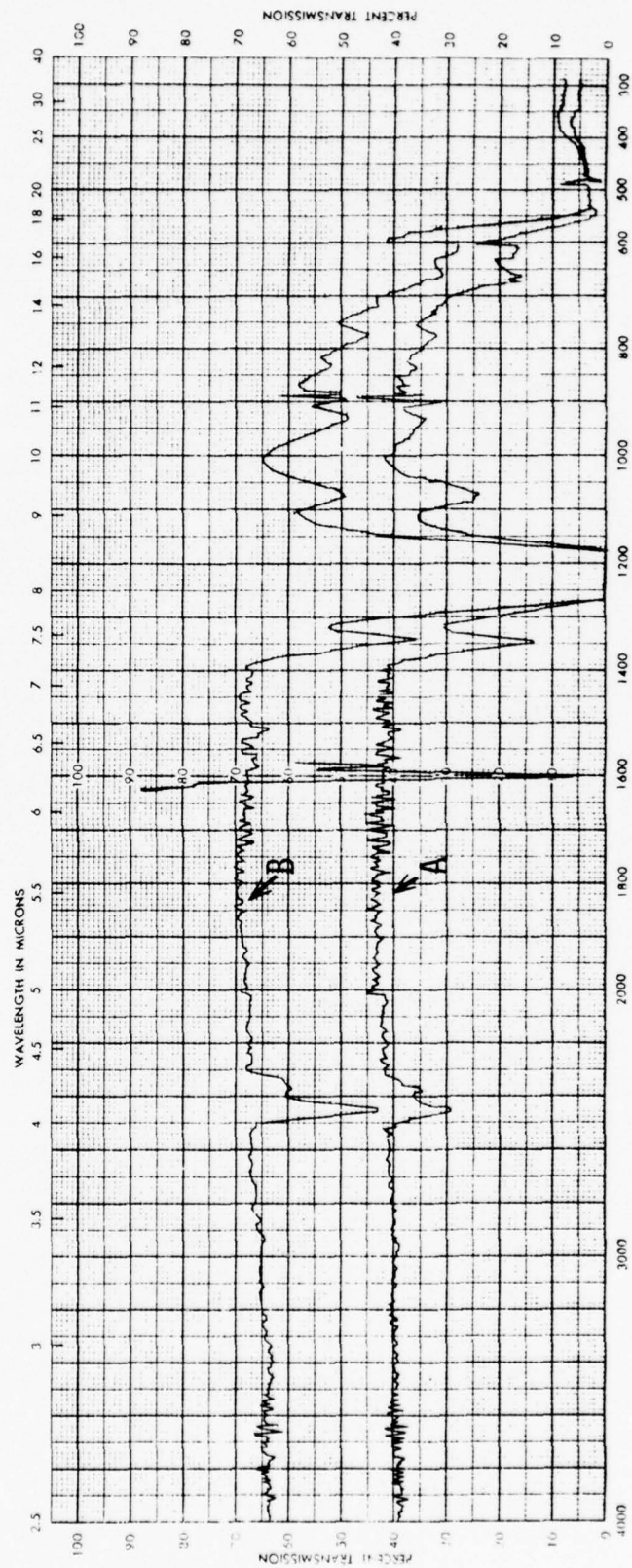
Fig. 13. IR spectra of SOCl$_2$-extract of cell materials after tests. (A) from cell C-6, (B) from cell P-5.

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from an anode limited Li/SOCl$_2$ cell which had been tested in a slightly floaded configuration.* The cell is shown in Figure 12 and the IR spectrum is shown in Figure 14. This spectrum also shows the peak at 1070 cm^{-1}. The other peaks in the spectrum, can be assigned to SO$_2$ and SOCl$_2$ (LiAlCl$_4$ electrolyte). We are currently making further investigations along these lines so as to determine whether the compound exhibiting the peak at 1070 cm^{-1} is formed during discharge or overdischarge.

Another prismatic cell, P-19 was discharged without Li on the anode grid. This cell represents an extreme case of anode limited configuration. During discharge, the reactions are oxidation at the anode and reduction at the cathode, situations similar to forced overdischarge in anode limited cells. This configuration should eliminate secondary reaction of the products of overdischarge with Li as would be possible in a normal anode limited configuration. The electrolyte from the prismatic cell (Fig. 15) was analyzed after a discharge of 0.70 Ah (0.56e$^-$/SOCl$_2$). The spectrum is shown in Figure 16.

In addition to the peaks present in Figure 14, the spectrum shows additional peaks at 1410 cm^{-1} (SO$_2$Cl$_2$) and 1110 cm^{-1} (SOCl$^+$ AlCl$_4^-$). We have previously identified SO$_2$Cl$_2$ and SOCl$^+$ AlCl$_4^-$ as oxidation products of SOCl$_2$/LiAlCl$_4$ in half cell studies (8). This is the first time that these products were identified in a cell of practical configuration. The reasons for these products not being present in the overdischarged cell shown in Figure 13 are presently under investigation.

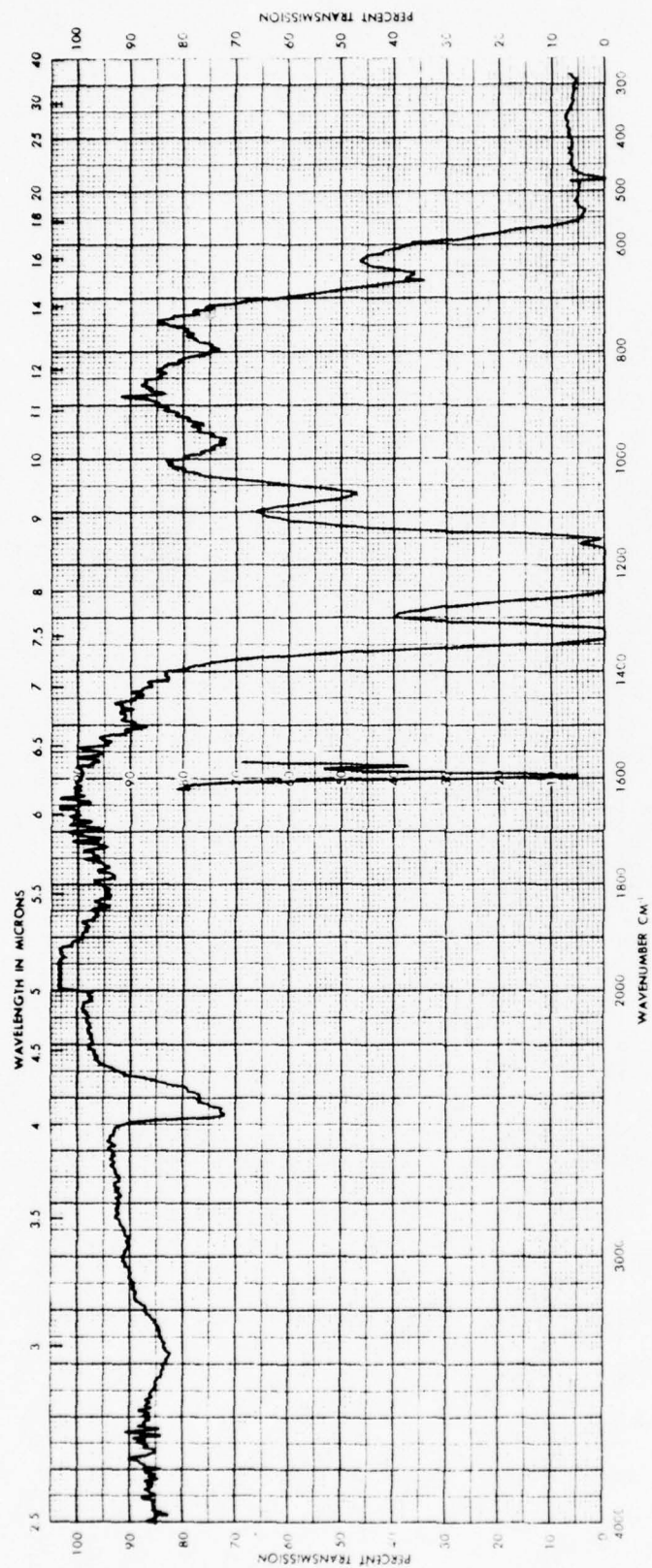*The excess of electrolyte was necessary to have electrolyte left for analysis after the test.

Fig. 14. IR spectrum of electrolyte from cell P-18 after the overdischarge shown in Fig. 13.
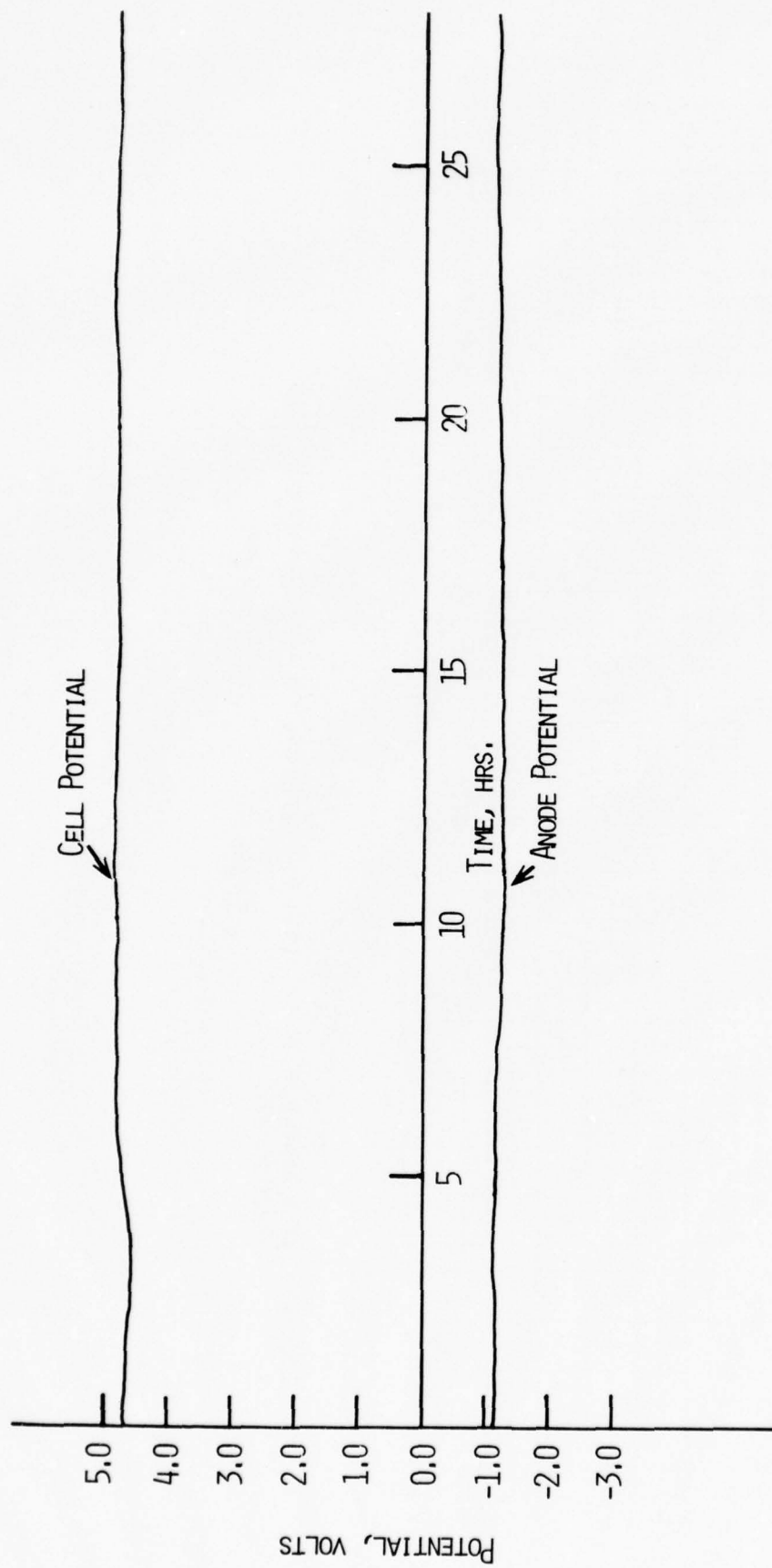
Fig. 15. Galvanostatic discharge curve for Li/SOCl$_2$ cell P-19. Current = 12 mA.
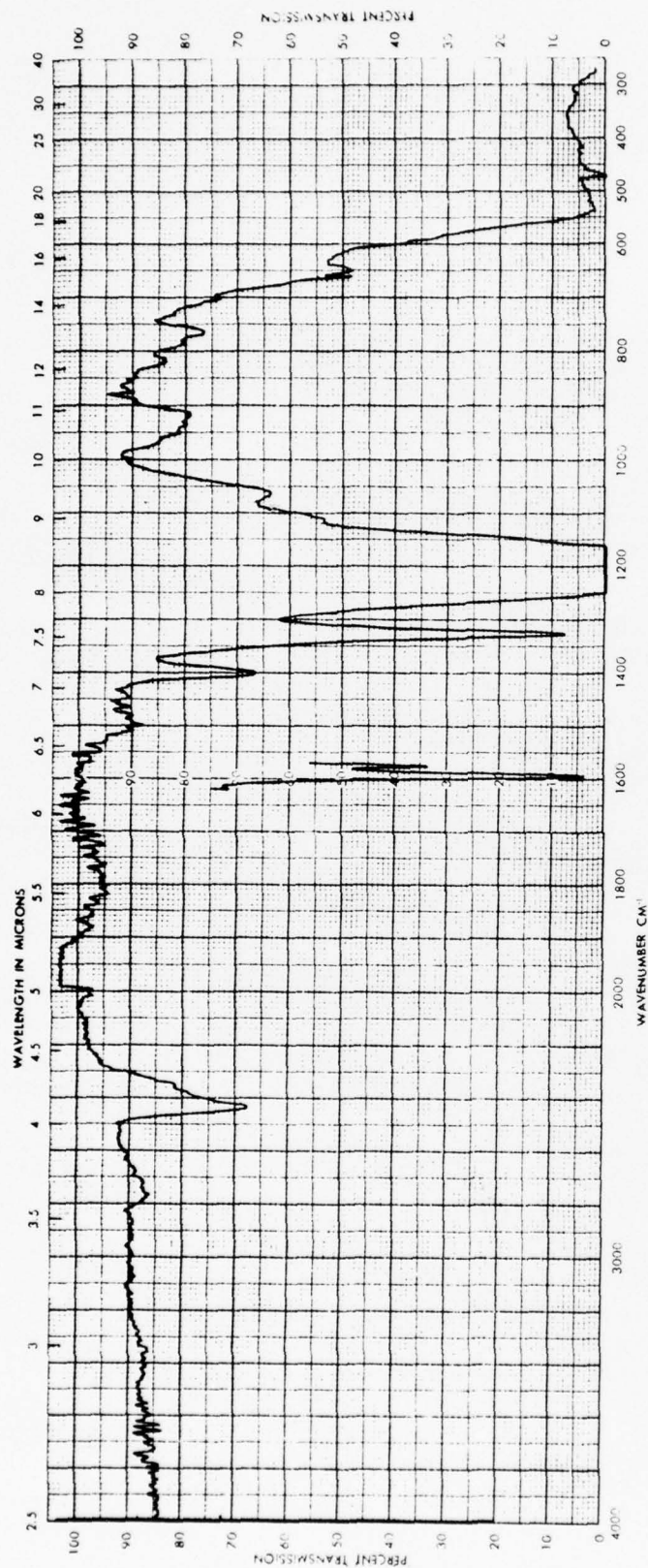
Fig. 16. IR spectrum of electrolyte from cell without Li on the anode (Cell P-19). The spectrum was recorded after discharge corresponding to 0.3 Ah.

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III.   BEHAVIOR OF Li/SOCl$_2$ CELLS ON CHARGING

1.   Experimental Results

It has been alleged that Li/SOCl$_2$ cells explode or charging, although no clear documentation is found in the literature. We have studied the charging behavior of five Li/SOCl$_2$ cells. Four of these were C-size cells, C-10, C-12, C-13 and C-14, and their charging behavior was examined as a function of the state of discharge of the cell as well as the concentration of LiAlCl$_4$. The fifth one was a small prismatic cell, P-15 and the electrolyte in this cell was that based on Li$_2$O/AlCl$_3$. The parameters for the C cells are shown in Table 4 and those of the prismatic cell are given in Table 3.

Cell C-10 was charged at 100 mA (0.60 mA/cm^2 of Li electrode area). The results are shown in Figure 17. The internal temperature, the cell potential and the potential of the anode vs. a Li reference electrode were measured.   The charge proceeded with the cell potential at 4.1V and the anode potential at -0.1V. The cell was charged for 97 hr (9.7 Ah) without change in cell polarization. The total charge passed exceeded both the Li and the SOCl$_2$ which were originally present in the cell in amounts of 7.4 and 7.37 Ah respectively. Open-circuit-voltage measurements after passing charges of 1.8 Ah and 4.4 Ah gave a value of 3.95V as opposed to the initial value of 3.65V. The cell internal temperature gradually increased to 31°C in a period of 4 hr and remained at this value during the entire test.

After charging, the cell was discharged again at 100 mA. The discharge is shown in Figure 18. The cell yielded a capacity of 3.95 Ah. Note that the initial 0.15 Ah of discharge occurred between 3.8 and 3.6V. This might correspond to the discharge of an accumulated product of charge, probably Cl$_2$. The cell was overdischarged also at 100 mA for 3 Ah and showed cathode limitation.

The important point to note is that the cell exhibited safe behavior during charge and the subsequent discharge and overdischarge.

Cell C-12 was initially discharged at 100 mA (Fig. 19) for 2 Ah. The OCV at this stage was measured to be 3.65V. The cell was then charged for 5.3 Ah also at 100 mA. The charging cell voltage remained at 3.7V for 35 hr (3.5 A) and then at 3.8V for the rest of the charging. The discharge of C-12 after the charge gave an additional capacity of 2.5 Ah, making the total discharge capacity of the cell to be 4.5 Ah, identical to that from a fresh cell. C-12 was overdischarged for 2 Ah, then charged for 2Ah. Discharging the cell after this last charge did not result in any capacity.

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TABLE 4

CELL PARAMETERS FOR Li/SOCl$_2$ CELLS TESTED FOR CHARGING BEHAVIOR

Cell No.	Carbon Electrode			Lithium Electrode		Electrolyte SOCl$_2$/1.8M LiAlCl$_4$		Discharge Current (mA)
	Average Thickness (mm)	Total Area (cm^2)	Amount of Carbon (g)	Total Area (cm^2)	Amount of Li (Ah)	Vol. (ml)	Capacity (Ah)	
C-10	0.68	194	1.65	166	7.4	12	7.4	100
C-12	0.64	184	1.74	166	7.4	12	7.4	100
C-13	0.71	184	1.78	151	6.72	12	7.5*	100
C-14	0.69	184	1.86	166	7.4	12	7.5	100

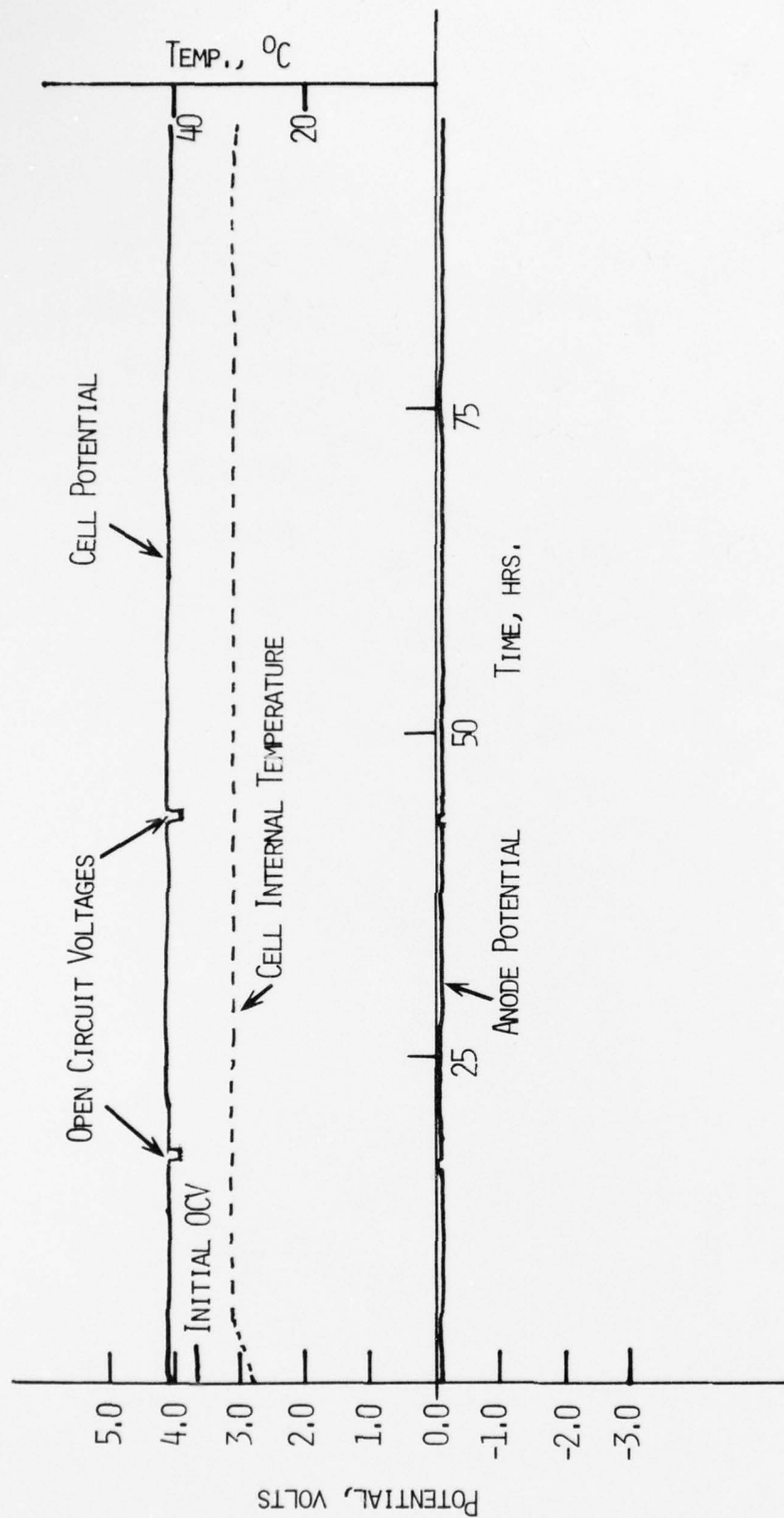*0.5M SOCl$_2$/LiAlCl$_4$ electrolyte.

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Fig. 17. Galvanostatic "charging" curve for Li/SOCl$_2$ cell C-10. Current = 100 mA.
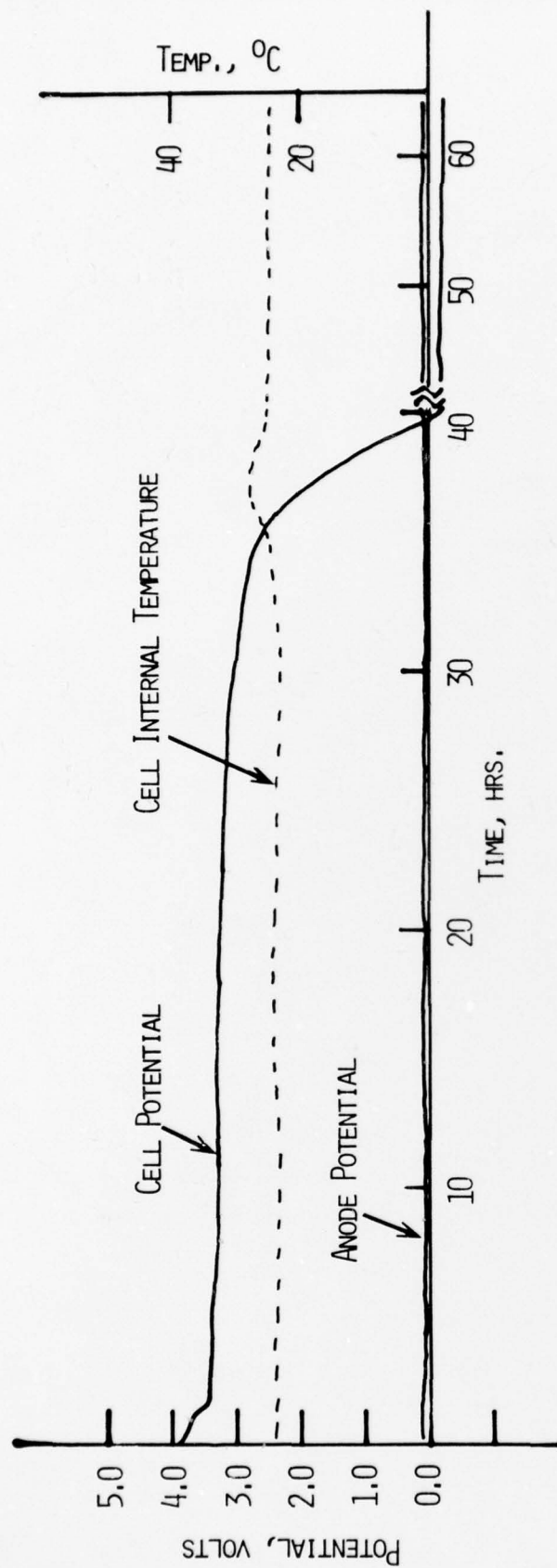
Fig. 18. Galvanostatic discharge and overdischarge curves for $Li/SOCl_2$ cell C-10 after the "charging" shown in Fig. 16. Current = 100 mA.
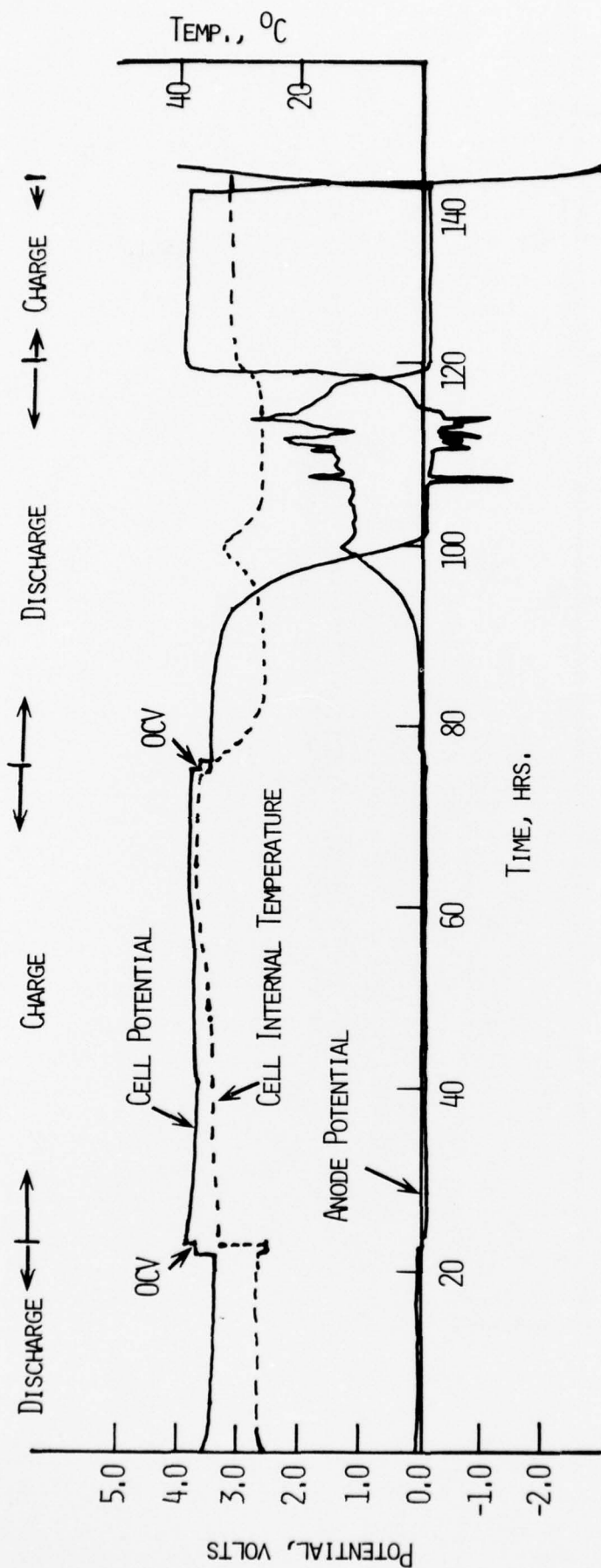
33

Fig. 19. Galvanostatic discharge and "charge" curves for Li/SOCl$_2$ cell C-12. Current - 100 mA.

The effect of concentration of LiAlCl4 on charging was investigated in cell C-13 and C-14 utilizing 0.5M LiAlCl4/SOCl2 solutions. Cell C-13 was charged at 100 mA for 92 hr (9.2 Ah), Figure 20. It was then discharged, again at 100 mA. The cell capacity to zero volt was 2.3 Ah. The discharge capacity was lower than what was obtained in C-10, tested similarly.
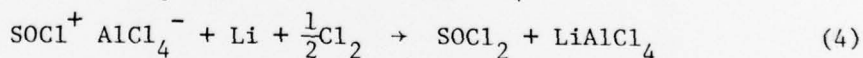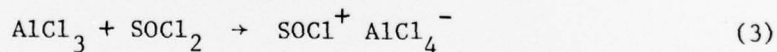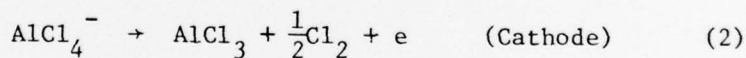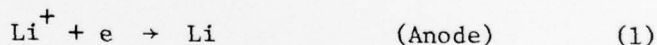
Cell C-14 also utilized 0.5M LiAlCl4/SOCl2 electrolyte. The cell was tested at 100 mA and the results are shown in Figure 21. After 70 hr of charging, the cell was discharged yielding a capacity of 2.85 Ah. The voltage profiles of C-13 and C-14 are similar to that found in cell C-10.

The charging behavior of Li/SOCl2 cells utilizing $Li_2O/AlCl_3$ based electrolyte was briefly investigated in cell P-15. This was a small prismatic cell and its parameters are given in Table 3. The behaviour during charging and subsequent discharging, shown in Figure 22, are similar to that of cells utilizing LiAlCl4/SOCl2 electrolyte. Better understanding of the mechanisms of charging in these types of cells should await more studies.

2.   Summary and Discussion

The charging behavior of Li/SOCl2 cells was studied using C-size cells. These cells could be "charged" for long periods of time without explosions. In fresh C-cells at 100 mA current, the "charging" proceeded at 4.1V. The cell voltage remained steady at this value even after passing an amount of charge exceeding $2e^-/SOCl_2$. When the cells were discharged after "charging" they yielded capacities comparable to that from fresh cells. These observations suggest that "charging" of Li/SOCl2 cells involve regenerative cell process, probably comprising both redox and chemical reactions.

A possible series of reactions during "charging" is shown in Equations 1-4.

$$Li^+ + e \rightarrow Li \qquad \text{(Anode)} \qquad (1)$$

$$AlCl_4^- \rightarrow AlCl_3 + \tfrac{1}{2}Cl_2 + e \qquad \text{(Cathode)} \qquad (2)$$

$$AlCl_3 + SOCl_2 \rightarrow SOCl^+ AlCl_4^- \qquad (3)$$

$$SOCl^+ AlCl_4^- + Li + \tfrac{1}{2}Cl_2 \rightarrow SOCl_2 + LiAlCl_4 \qquad (4)$$

The $LiAlCl_4$ that is electrolyzed according to the redox reactions 1 and 2 and it is regenerated in the chemical reaction 4.
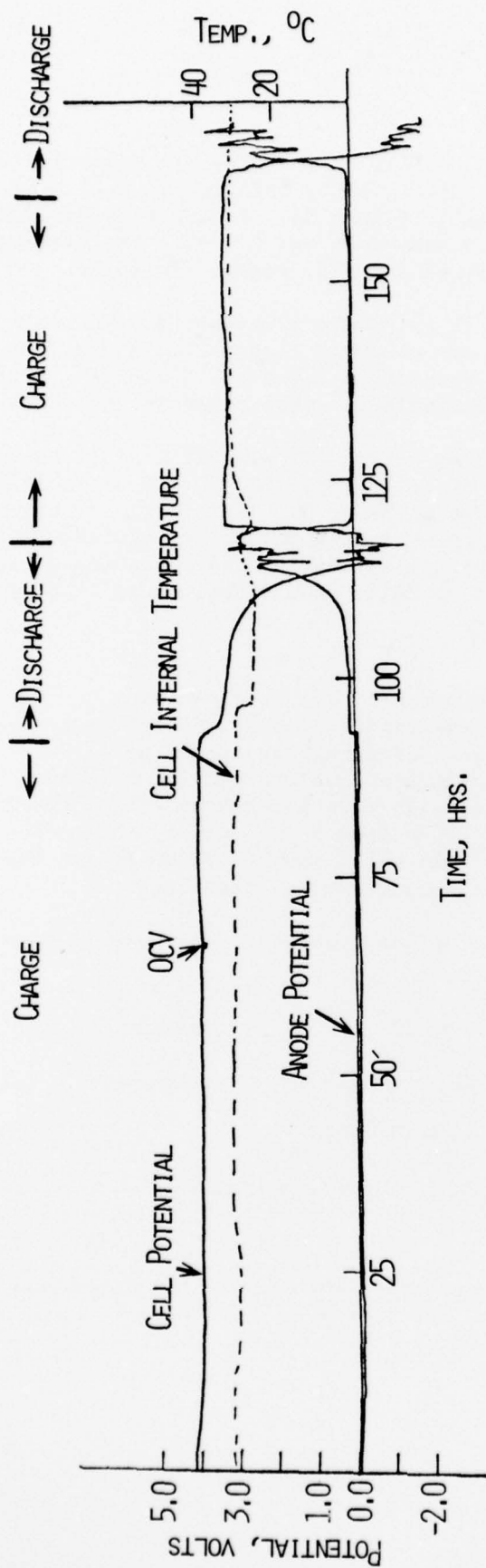
Fig. 20. Galvanostatic "charge" and discharge curves for cell C-13. Current = 100 mA.
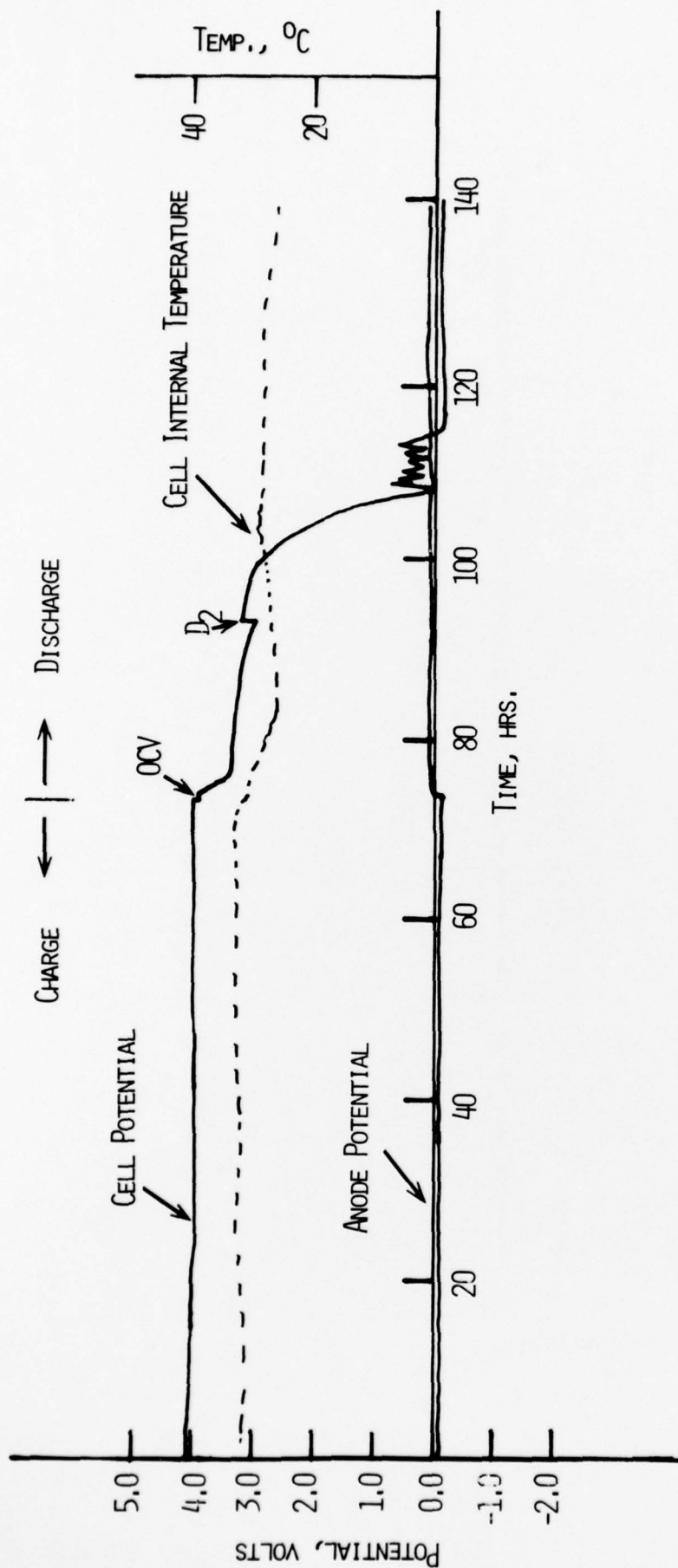
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Fig. 21. Galvanostatic "charge" and discharge curves for Li/SOCl$_2$ cell C-14. Current = 100 mA. At D$_2$ current reduced to 50 mA.
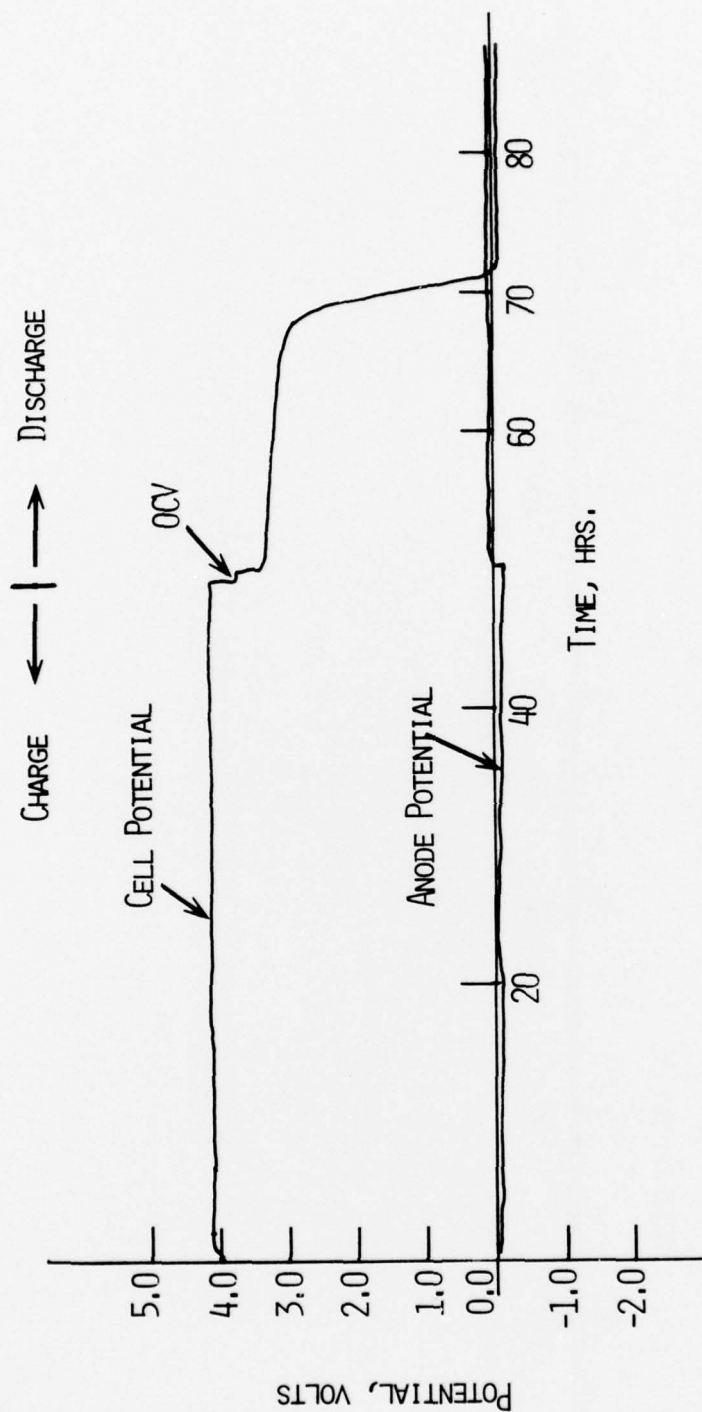
Fig. 22. Galvanostatic "charge" and discharge curves for Li/SOCl$_2$ cell P-15. Current = 36 mA.

The charging behavior resembled the discharge characteristics of Li/SOCl$_2$ cells without Li on the anode Exmet (8).

The "charging" of a partially discharged cell proceeded at lower potentials, i.e., $\sim$3.8V when the test current was 100 mA. This cell also did not exhibit a change in cell polarization even after long periods of "charging". Moreover, it was possible to discharge the cell after the "charging" and the total discharge capacity was identical to that from fresh cells. A possible reason for lower "charging" potentials in partially discharged cells is the "activation" of the carbon cathode so that the same regenerative reactions occurring in fresh cells occur at lower voltages. However, a different set of reactions cannot be ruled out. We are currently investigating this.

The charging behavior of cells utilizing 0.5M LiAlCl$_4$/SOCl$_2$ solutions was identical to those utilizing 1.8M LiAlCl$_4$/SOCl$_2$ solutions. However, the discharge capacities after the "charging" was lower in cells with the lower salt concentration. It is interesting to note that both types of cells were built for cathode limitation. But one of these cells utilizing lower salt concentration showed anode limitation. The latter behavior might be related to the "charging" prior to the discharge. The "charging" probably affects the Li anode more when the salt concentration is lower. This aspect is under investigation.

The behavior of a cell utilizing Li$_2$O/AlCl$_3$ based electrolyte was similar to those utilizing LiAlCl$_4$, both during charging and subsequent discharging.

All the cells tested exhibited safe behavior during the charge and the subsequent discharge and overdischarge.

IV. SUMMARY AND FUTURE WORK

Forced overdischarge behavior of Li/SOCl$_2$ cells was studied using C-size and small prismatic cells. These cells were either cathode or anode limited. Cathode-limited cells could be overdischarged for long periods of time without explosions. Internal temperature measurements indicated that the overall temperature in cathode limited C-cells during most of the discharge and overdischarge was close to that of the ambient. A slight peaking of the temperature was observed when the cathode polarized rapidly at the end of useful cell-life.

Forced overdischarge of one anode-limited C-cell tested at 100 mA resulted in explosion. Internal temperature measurements did not reveal any significant differences from cathode limited cells. Analysis of spent electrolyte from overdischarged cells showed the presence of a material exhibiting IR absorption at 1070 cm^{-1}. The material has not yet been identified. The compounds SO$_2$Cl$_2$ and SOCl$^+$ AlCl$_4^-$ were also shown to be products in overdischarged anode limited cells.

Studies of the charging behavior of Li/SOCl$_2$ cells showed that these cells could be charged for long periods of time without any change in cell polarization. It was also found that the full capacity of the cell could be recovered in the discharge following a long charging utilizing an amount of charge greater than the amount of either Li or SOCl$_2$ originally present in the cell. The behavior was indicative of charging reactions involving regenerative processes. The charging of Li/SOCl$_2$ cells did not appear to be hazardous.

During the next quarter, work will concentrate on analytical studies using IR, cyclic voltammetry and wet methods, aimed at understanding the chemical processes involved in forced overdischarge and charge of Li/SOCl$_2$ cells.

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